SPRAY LAYER-BY-LAYER OPTICAL COATINGS

An Undergraduate Research Scholars Thesis

by

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ABSTRACT

Spray Layer-by-Layer Optical Coatings. (May 2015)

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Polymer thin films are contributing to many fields today, with Bragg reflectors being one of them. Bragg reflectors can be used in many optical instruments and experiments, as well as practical applications like keeping cars cool in the sun[1]. Here, the production of robust Bragg reflectors with tunable properties is explored using spray layer-by-layer assembly and novel materials. In order to do this, the growth rate of the polyelectrolyte complex to be used, polyethylene oxide and poly(methacrylic acid), will be profiled. Spray deposition of gold nanoparticles will also be studied. If successful, this process could possibly lead to rapid, scalable production of Bragg reflectors for cheaper, widespread use.

NOMENCLATURE

Layer-by-Layer: LbL

Poly(Methacrylic acid): PMAA

Poly(Ethylene Oxide): PEO

Poly-(glycidyl methacrylate): PGMA

Indium Tin Oxide: ITO

Deionized: DI

Gold Nanoparticles: AuNPs

Transmission Electron Microscope: TEM

CHAPTER I

INTRODUCTION

Bragg reflectors are a form of dielectric mirror which are highly tunable. They are made with multiple layers of various types and thicknesses of dielectric materials. By adjusting those production variables, the reflectivity can be controlled as well as which specific wavelengths of light are reflected. These Bragg reflectors are useful for applications in optics such as lasers, beam splitters, and fluorescence microscopy, among other things. The production of these mirrors is usually done via ion beam, chemical vapor, physical vapor, and sputter depositions [2].

The subject of my research is a relatively new production method for Bragg reflectors; Spray assisted LbL assembly. LbL assembly is a process of depositing polymer thin films by alternating exposures of two different polymer systems. The two different polymers are complementary in some way, like hydrogen bonding or polyion interactions, which lead to mutual attraction and film build up [3]. The type of complex to be used will be a system of polyelectrolytes that hydrogen bond to hold the layers together. The research already done has used silicon dioxide and titanium dioxide as the dielectric materials and PDAC/PSS as the polymer complex. It succeeded producing working Bragg reflectors in various ranges, ranging from visible light, to infrared [1].

Bragg Reflectors

Bragg reflectors, also called Bragg mirrors, work by using layer pairs of two optically different materials [4,5]. These layer pairs need to make a heterogeneous film, with each layer being a

single phase of material. This is different from normal LbL films in which the entire film is essentially homogenous even though it is two different layers being added for each bi-layer. In this research, I will be using the PEO/PMAA complex as one optically homo layer, and a layer of gold nanoparticles as the second homo layer. One of the most common types of reflector made is a quarter-wave mirror in which each optical layer has a thickness a fourth the length of the wavelength being reflected [4]. The reason two separate types of optical materials are required is the interface between them. This interface causes a phenomenon known as Fresnel reflection, which causes light to change its path due to the difference of refractive indices in the two materials. If properly assembled, each layer pair reflects light that causes constructive interference with one another. As a result, the more layer pairs there are, the higher the reflectivity of the overall mirror [5].

Dielectric mirrors are one type of mirror that can be produced from Bragg reflectors. They can either be a simple Bragg reflector themselves, or they can have more complicated structures made of combinations of reflectors. A complicated dielectric mirror can be used to reflect multiple ranges of wavelengths and achieve broader bandwidths. This tunable reflectivity is what makes dielectric mirrors the primary reflectors used in lasers. High reflectivity is desired for the closed end mirror, which can be achieved through increasing the number of layer pairs. Partial transmission is needed for the exit mirror in the laser so the reflectivity is reduced. This tunable property allows for reflectors called supermirrors to be produced, which have recorded reflectivities of greater than 99.99999% [6].

CHAPTER II

METHODS

Materials

The main materials used in experimentation were the following polymers from Polysciences: poly(methacrylic acid) (Mw = 100 000 g/mol) and Poly(ethylene oxide) (Mw = 100 000 g/mol). Poly-(glycidyl methacrylate) (Mw= 25 000 g/mol) was used in substrate preparation. These three polymers were purchased from PolySciences. The substrates used were indium tin oxide coated glass slides purchased from Delta Technologies Limited.

Solution Preparation

All solutions directly used in the process of spray coating all need to be the same pH, which in my case is pH 4. Both the PMAA and PEO solutions were made to be 20 mM based on molecular weight of the repeat units. These solutions and DI water are brought to pH 4 using a pH meter calibrated with 4, 7, and 10 pH buffers. In order to alter pH, sodium hydroxide and hydrogen chloride are used dropwise.

Substrate Preparation

The ITO slides are first cleaned using a basic piranha solution made of 17 mL of DI water, 3.4 mL of hydrogen peroxide, and 3.4 mL of ammonium hydroxide. The slides are placed into the solution and heated in a hot bath to 75°C for 20 minutes. They are then rinsed with more DI water and sonicated for 5 minutes before drying with compressed air or nitrogen. Next, the slides are oxygen plasma treated for 5 minutes. The ITO slides are then dipped in 0.1% PGMA/methyl

ethyl ketone solution for 3 minutes and brought to 110 °C for 30 min. Once cooled to room temperature, excess PGMA is removed via a methyl ethyl ketone rinse. The now coated slides are dipped in 20 mM PMAA solution for 20 minutes before being removed and heated on a hotplate for 30 minutes at 110 °C. The final coated substrates need to be rinsed in the proper pH DI water before use to remove excess PMAA[7].

Spray LbL Assembly

In order to produce my thin film samples, an automated spraying system from Svaya Nanotechnologies was used. In order to ensure clean and clear nozzles, pH 4 water is sprayed through each nozzle for a minute at 60 psi. The prepared substrates are placed on the rack in the system about 20 cm away from the nozzles and the first few sprays should be observed to ensure centering. The system is then set to 40 psi and the solutions are loaded. For a normal bi-layer, PEO is sprayed for 10 seconds, then left to drain for 10 seconds. Water is then sprayed for 10 seconds to rinse the sample and once again is left to drain for 10 seconds. PMAA is then sprayed for 10 seconds also with the 10 second drain. After another spray and drain of water, the bi-layer is complete. In order to add a layer of nanoparticles, the PMAA layer is replaced with the nanoparticle solution. For consistent growth in samples, be sure all solution used is the same pH[7].

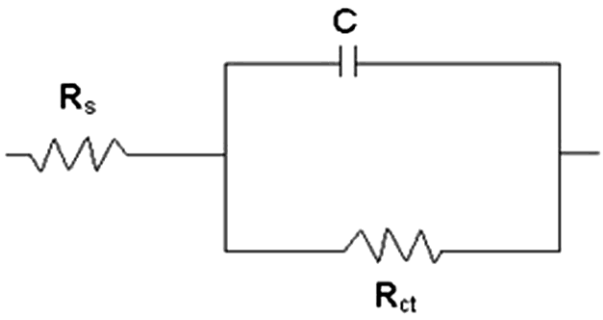
Characterization

In order to find the films' thicknesses profilometry is done using the KLA -
Tencor Instruments P-6 profilometer. The film is scratched using a razor and using step height measurements to find the thickness from the top of the film to the top of the substrate. Multiple

measurements should be made and averaged to find the overall thickness and standard deviation [7].

UV-Vis spectroscopy was performed using the SolidSpec-3700 UV-VIS NIIR spectrophotometer from Shimadzu. The reference was first taken using a clean, unused ITO slide, then the measurements of the samples were taken.

Impedance spectroscopy was done with a Gamry 1000 in two terminal cell tests. A vacuum of ~50 mmHg was pulled in order to ensure no water was present in the measurements. This vacuum and the measurements themselves were done inside a vacuum oven which doubled as a faraday cage to prevent outside interference. The conductive side of the indium tin oxide glass substrates was used as one electrode with copper tape on top of the film as the other electrode. A Randles equivalent circuit was used to convert raw impedance data to conductivity.



$$\sigma = \frac{L}{R_{ct}A}$$

Figure 1. (Left) Randles equivalent circuit [8] (Right) Conductivity equation using R_{ct} gathered from impedance data and Randles, L from profilometry, and A from the electrode cross-sectional area.

CHAPTER III

RESULTS AND DISCUSSION

The three main qualities that were assessed in this investigation were the film growth, the optical absorbance properties, and the conductivity of the films. The film growth assessment showed two different linear growth periods. The first is slightly lower and known as the inductance period, the second is a much higher, linear growth that results from the polymer system being firmly connected to the substrate. The low then high linear growth that looks somewhat exponential is characteristic of LbL assembly [9]. The UV-Vis spectra showed peaks corresponding to the nanoparticles introduced to the films, the larger number of nanoparticle layers corresponds with higher absorptivity in the same peaks. Due to the conductive nature of the nanoparticles used, the conductivities of the whole films themselves were tested. The results showed that the films had high resistances, except in cases where the nanoparticles may have penetrated their separating layers.

Film Growth

The film growth profiles performed showed relatively linear growth even though it was determined that the spray LbL assembler was clogged for a good portion of the process. The clog reduced the amount of PMAA flow to the sample and resulted in a large amount drying when the process should be wet between most steps. This reduced amount of PMAA and the possible drying may have led to the irregular growth and extremely high roughness seen in the growth profiles' samples. While the growth was disturbed, the growth profile still serves as a relatively accurate representation due to its somewhat linear nature and the non-profile samples reflecting

similar thicknesses. From extrapolation via trendline, the growth is estimated to be about 6 nm per bi-layer of PEO/PMAA.

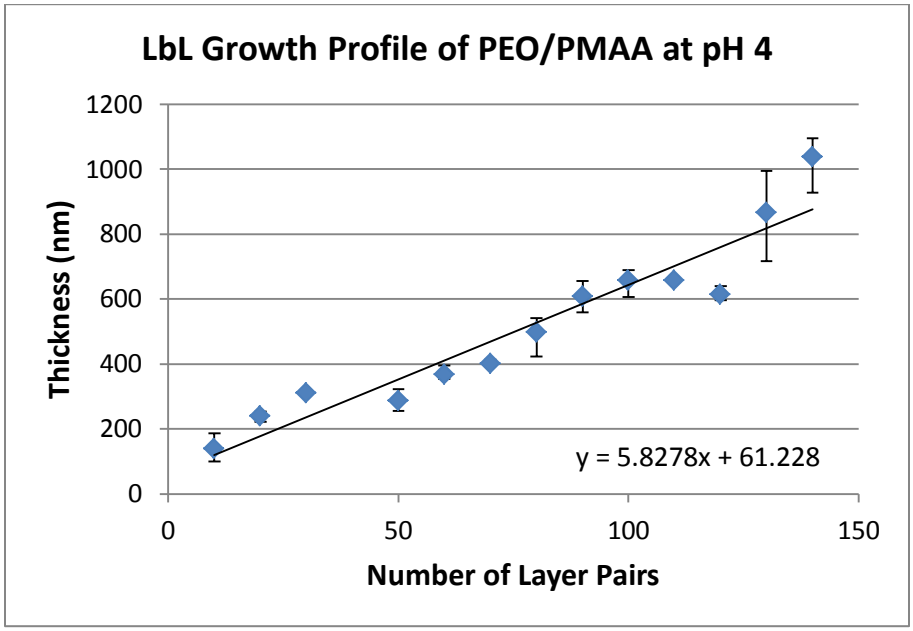


Figure 2. Dry film thickness of spray LbL assemblies of PEO/PMAA at pH 4 measured using profilometry.

UV-Vis Spectroscopy

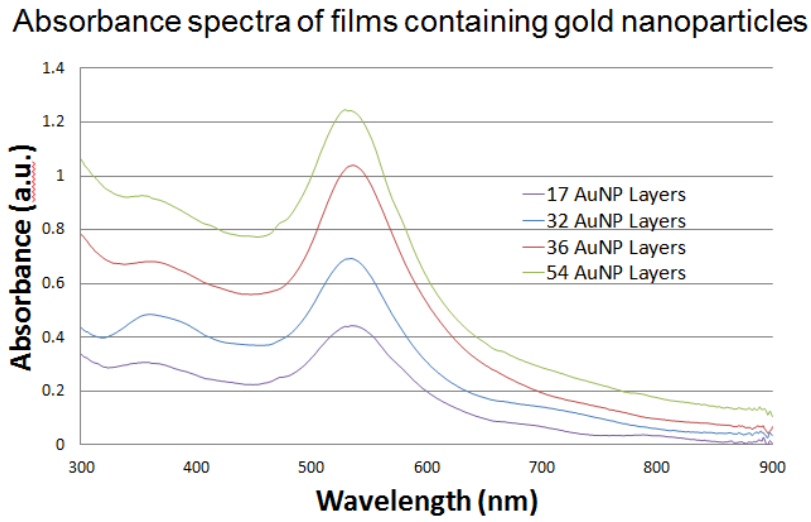


Figure 3. Absorbance spectra for PEO/PMAA films containing increasing numbers of discrete gold nanoparticle layers

The absorbance spectra gathered for the samples all keep parallel paths except for some shifting in the high frequency range due to substrate interference. The number of bi-layers between each layer of gold nanoparticles is constant so more gold layers do not mean an increased volume fraction of gold. The main absorption peaks can be seen in the 500-600 nm range which corresponds to our AuNP sizes of 15-20 nm [10]. The goal of increasing gold layers was to see a peak red-shift due to increased amounts of plasmonic optical tuning [11]. The only result shown is that as gold layers increase, more nanoparticles are present to absorb more light.

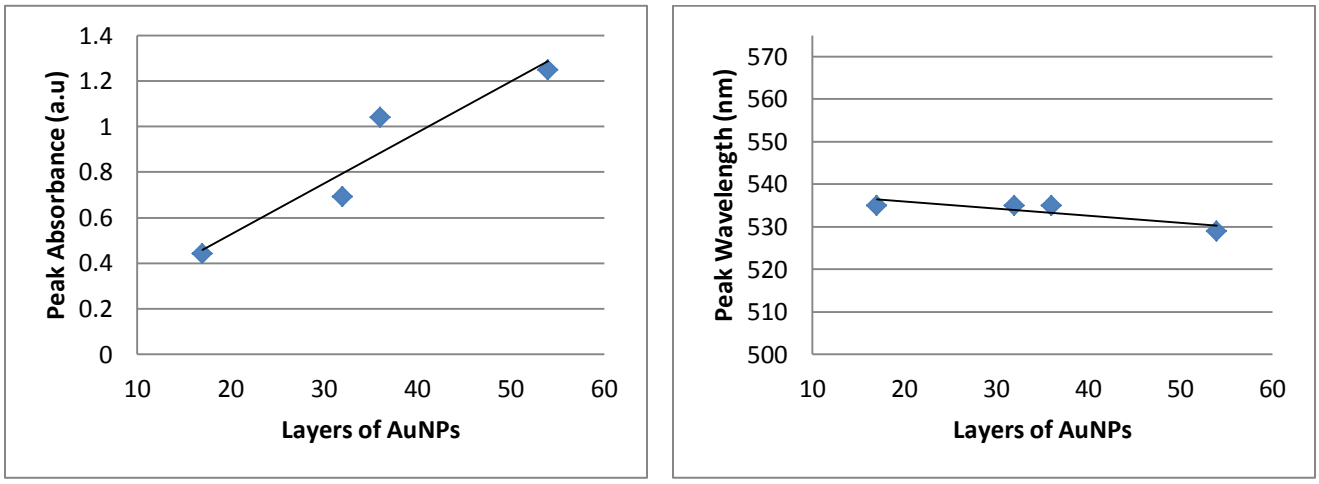


Figure 4. (Left) Peak Absorbance vs Layers of AuNPs (Right) Peak Wavelength vs Layers of AuNPs

From figure 4 you can see that the peak absorbance grows in a relatively linear fashion with increased gold layers. Figure 4 also shows that even with this increase in gold layers, the absorbance spectra peak at nearly the same wavelength. This constant peak leads to the conclusion that the gold nanoparticles are depositing in the same fashion throughout the films. A possible reason for the lack of plasmonic coupling can be seen in TEM imaging. Plasmonic coupling requires a very small distance between particles to have a large enough effect to be noticeable [12]. It can be seen in figure 5 that most nanoparticles are more than their average

diameter away from any other particles. The goal of having discrete layers of the nanoparticles was reached with relative success. After the LbL growth passed its induction period, distinct layers were observed. The curves in the layers may be due to the microtoming process used in TEM imaging not having a working cryomicrotomer. Another reason could just be irregular growth areas on the film.

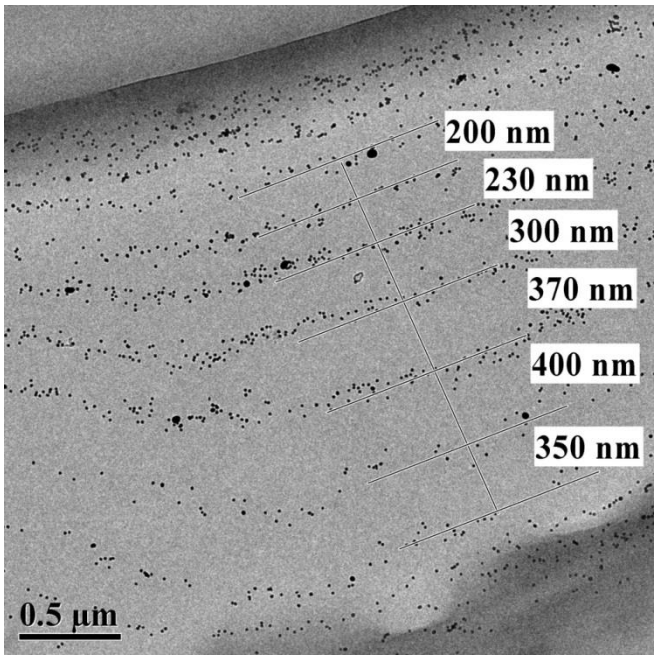


Figure 5. Cross sectional TEM image of a PEO/PMAA LbL film with introduced gold nanoparticle layers. The labeled lengths are the distances between gold layers.

It can also be seen in figure 5 that the distance between gold layers increases even though the number of bi-layers used between them is constant. This supports LbL films starting with a slow growth induction period then increasing growth per bi-layer until linear like the last three distances labeled.

Conductivity

Besides attempting bragg reflection, another purpose of having the polymer layers between the nanoparticles is to have an insulating effect. Impedance spectroscopy taken across the film perpendicular to the substrate plane showed conductivities below 1E-10 S/m. Even though instrument limitations prevented more accurate conductivities from being recorded, it was enough to confirm that the films were highly insulative.

CHAPTER IV

CONCLUSION

In summary, spray LbL techniques demonstrated the ability to produce discrete layers of gold nanoparticles in thin films of PEO/PMAA at pH 4. The growth rate of PEO/PMAA spray LbL deposition was measured to be about 6 nm per bi-layer. The growth profile this was taken from was known to have equipment errors but the growth rate is still useful for rough calculations. A new growth profile needs to be done in order to improve accuracy and decrease roughness in the profile. UV-Vis spectroscopy revealed that our increasing introduction of discrete gold layers did not lead to peak red-shifts from plasmonic coupling. The peak absorbance increases linearly with gold deposition. Peak wavelength stays constant with gold deposition meaning the gold nanoparticles deposit the same way in the different samples. Aggregation of the nanoparticles would have led to a red-shift in the absorbance wavelength, which was not observed [13]. It was desired to have films with insulative properties perpendicular through the film. This aspect was a success with impedance spectroscopy revealing conductivities below 1E-10 S/m.

Future Work

New growth profiles can be produced to have a more accurate representation of film growth and possibly growth at different pH ranges. Increasing the concentration of gold nanoparticles used in spraying might decrease the distance between each individual particle in the discrete layers. This could possibly bring about plasmonic coupling or order the layers more for bragg reflection. Since conductivity in the perpendicular direction has been done, parallel conductivity could be measured by using a four point probe [14]. Parallel conductivity could be quite different if

current travels down the length of the film parallel to the substrate due to the layers of gold nanoparticles. Different nanoparticles like polyaniline nanofibers are already being characterized to see if they have improved performance over the gold nanoparticles.

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